

Mechanisms of Hydrogen Donation from Cyclic Olefins
to Pittsburgh No. 8 Coal

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INTRODUCTION

Hydrogen donation is considered to be an important mechanism by which hydrogen is transferred from the solvent to coal during coal liquefaction (Bockrath, 1982). Hydrogen donation from cyclic olefins such as 1,4,5,8,9,10-hexahydroanthracene (HHA) and 1,4,5,8-tetrahydronaphthalene or isotetralin (ISO) to coal has been shown to be both rapid and effective (Bedell and Curtis, 1991). This investigation examined the mechanisms and kinetics by which HHA and ISO transfer their hydrogen to Pittsburgh No. 8 coal and compared these effects with those of hydroaromatic donors. The cyclic olefins readily converted to hydroaromatics at liquefaction conditions but still remained more effective than most conventional hydroaromatic donors in converting coal. Combinations of cyclic olefins and conventional hydroaromatic donors produced effective hydrogen donor combinations providing hydrogen rapidly and sustaining hydrogen donation throughout the reaction time. The universality of the effectiveness of the cyclic olefin donation was examined with a set of eight coals from the Argonne Premium Coal Bank that are of different rank and reactivity. The cyclic olefins effectively converted the coals of different rank, being most effective with the coals of intermediate reactivity.

Efficient coal liquefaction processing requires that hydrogen be transferred to the dissolving coal matrix at the rate that it can be accepted by the reacting coal molecules and effectively used donors. A key to obtaining high coal conversion in liquefaction through donation from solvent is the matching of the rate that hydrogen is released by the donor and accepted by the coal. When these rates are not matched, inefficient usage of the hydrogen results. When hydrogen is released by the donor too quickly, the hydrogen is not used by the dissolving coal and forms gaseous hydrogen; when hydrogen is released too slowly, retrogressive reaction of the dissolving coal molecules can occur forming refractory coke precursors.

The goals of this research were to evaluate the effects of different rates of hydrogen donation by evaluating the hydrogen donation from a cyclic olefin, 1,4,5,8,9,10-hexahydroanthracene (HHA) in combination with the hydroaromatic, 9,10-dihydroanthracene (DHA). The acceptor used in this study was Pittsburgh No. 8 coal. Liquefaction reactions were performed with the combined donor system as well as with individual cyclic olefins, HHA and ISO, and hydroaromatic donors, DHA, octahydroanthracene (OHA) and tetralin (TET). The rate of hydrogen acceptance by Pittsburgh No. 8 coal was determined in terms of coal conversion to THF solubles after different reaction times.

These same hydrogen donors were evaluated with eight coals from the Argonne Premium

Coal Sample Bank. These coals were of different rank and reactivity. The various degrees of hydrogen acceptability and, hence, reactivities of the coals were evaluated.

EXPERIMENTAL

Reactions with Pittsburgh No. 8 Coal. The reactions of cyclic olefins, HHA and ISO, and hydroaromatic donors, DHA, OHA, and TET were performed with Pittsburgh No. 8 coal from the Argonne Premium Coal Sample Bank. Information concerning Pittsburgh No. 8 coal properties is given in Table 3. Reactions were performed in 50 cm³ stainless steel tubular reactors that were agitated at 700 cpm. The reaction conditions used were 30 minutes reaction time, 1250 psig H₂ atmosphere at ambient temperature, 380°C reaction temperature, 2.0g coal, 4.0g total solvent mixture including 0.5 weight percent donable hydrogen of the donor with the balance being hexadecane as the diluent solvent.

Reactions with Argonne Coals. Reactions were performed with the hydrogen donors, both cyclic olefins and hydroaromatic donors, and eight Argonne Premium Sample Bank coals. Another coal, Western Kentucky No. 9, from the PSU/DOE sample bank was used for comparison. The reactions were performed using the same type of reactor and conditions as those with Pittsburgh No. 8 coal.

Materials and Analysis. The hydrogen donors used were obtained from the following manufacturers and were used as received: tetralin, 1,4,5,8,9,10-hexahydroanthracene, 1,2,3,4,5,6,7,8-octahydroanthracene, 9,10-dihydroanthracene, and hexadecane from Aldrich Chemical Co.; 1,4,5,8-tetrahydronaphthalene (isotetralin) from Wiley Organics Inc.; and Pittsburgh No. 8, Illinois No. 6, Upper Freeport, Pocahontas No. 3, Lewiston Stockton, Blind Canyon, Wyodak and Beulah Zap coals from the Argonne Premium Coal Sample Bank. Western Kentucky No. 9 coal was obtained from the PSU/DOE Coal Sample Bank.

The hydrogen donor compounds and their products produced during coal liquefaction were analyzed by gas chromatography using a Varian 3400 gas chromatograph equipped with a HT-5 column from SGE and FID detection. The internal standard method with biphenyl as the internal standard was used. The peaks were identified by comparing retention times with authentic compounds and by GC mass spectrometry using a VG 70EHF mass spectrometer.

Coal conversion is defined as

$$\text{Conversion} = [1 - [\text{IOM (maf)}] / \text{coal charge (maf)}] \times 100$$

where IOM is the THF insoluble organic matter remaining after reaction and maf is defined as moisture and ash free.

RESULTS AND DISCUSSION

Cyclic olefins, as donors for coal liquefaction, have been shown to release their hydrogen readily and quickly to the dissolving coal matrix. The conversion of cyclic olefins occurred very rapidly at liquefaction temperatures, forming a number of reactions products including

hydroaromatic and aromatic compounds (Bedell and Curtis, 1991). HHA converted quickly at temperatures of 380°C and above, forming reaction products of DHA, OHA, and anthracene (ANT). DHA has also been shown to be very effective in converting coal at liquefaction temperatures (Bedell, 1991); however, the conversion and subsequent release of hydrogen from DHA was not nearly as rapid as that from HHA. The purpose of this research was to investigate the possible synergism between the hydrogen donating rate of HHA and DHA on coal conversion. The idea being explored was that HHA released its hydrogen very quickly making it readily available to the coal as it initially began to dissolve while DHA released its hydrogen more slowly making hydrogen available to the less reactive components of the coal.

The reactions performed as shown in Table 1 were comprised of varying amounts of HHA and DHA. The reactions were configured to maintain a constant level of 0.5 weight percent donable hydrogen. Hence, the amount of donable hydrogen remained the same although the relative amount of each donor was varied from 75% HHA and 25% DHA to 75% DHA and 25% HHA. The reaction that produced the highest coal conversion to THF solubles contained equal levels of donable hydrogen from HHA and DHA. Nearly 12% more coal conversion was obtained from the combined HHA/DHA system than with HHA alone, while nearly 7% more conversion was obtained with the combined system than with DHA alone. The reactions containing 75% HHA and 25% DHA produced more coal conversion than the reaction with HHA alone, and nearly equivalent coal conversion as the reaction with DHA alone. The reaction containing 75% DHA and 25% HHA produced more conversion than either HHA or DHA alone.

These increases in coal conversion with the combined systems suggested that combining the two donors provided a synergism in both the amount and rate of hydrogen released in the system. Additional reactions were performed to evaluate the effect of time on the behavior of the hydrogen donors. Reactions were performed with the combined HHA and DHA system and with the individual donors of HHA, DHA, OHA, ISO and TET for reaction times of 5, 15, 30 and 60 minutes. Hydrogen donation was monitored by evaluating the reaction products from the donors. Hydrogen acceptance was measured by evaluating coal conversion to THF solubles. At the short reaction time of 5 minutes, HHA produced the most coal conversion, producing slightly more than the HHA/DHA combined system, 5% more than the DHA system, and 16% more than OHA. Analysis of the reaction products from hydrogen donors showed that more than 70% HHA converted while less than 25% DHA converted after 5 minutes of reaction. In the combined system, almost all of the HHA had converted after 5 minutes. Comparison of the cyclic olefin, ISO, to the hydroaromatic donor, TET, again showed much higher coal conversion at short reaction time. ISO converted very rapidly forming a reaction products of 1,2-dihydronaphthalene (DHN) and naphthalene (NAP) while TET remained essentially unreacted. These experimental results indicate that the rapid release of hydrogen by cyclic olefins promoted coal conversion at shorter reaction times compared to the slower hydrogen release by the hydroaromatic donors.

The liquefaction reactions of Pittsburgh No. 8 coal at 15, 30 and 60 minutes with the two types of donors are also compared in Table 2. At the short reaction time of five minutes, the cyclic olefin HHA produced the highest coal conversion to THF solubles. At longer reaction times of 15 and 30 minutes, the combined HHA/DHA reaction produced the highest coal

conversion. At the longest reaction of 60 minutes, the combined HHA/DHA and the individual DHA and HHA systems all produced similar coal conversions. Even in the system with no hydrogen donor present, the amount of coal conversion increased with time. Hence, coal conversion in a hydrogen atmosphere increased with time regardless of the presence or type of hydrogen donor present. However, the presence of the hydrogen donor increased the amount of coal conversion achieved by 13 to 22% at the long reaction time. Greater benefits were observed with some of cyclic olefin donors or the combined cyclic olefin/hydroaromatic donors at shorter reaction times.

Each of the hydrogen donors underwent reactions that released hydrogen from themselves. HHA showed the most reactivity while OHA showed the least amount of reactivity for the conversion of the donor to other species. In the reaction times of 15 minutes and longer, HHA formed OHA, DHA, and ANT; OHA formed DHA and ANT and DHA formed OHA and ANT. At short reaction time of 5 minutes, tetrahydroanthracene (THA) was observed in the individual reactions of OHA, HHA and DHA.

The reactions using the two ring donors, ISO and TET, yielded the same trends. ISO converted coal much more quickly than did TET and showed substantial increases in coal conversion compared to the amount produced by TET. However, at longer reaction times of 15 and 30 minutes, both ISO and TET showed similar coal conversion which was substantially more than without any donor. ISO was highly reactive forming TET and naphthalene (NAP) at reaction times of 15 minutes and longer, but forming 1,2-DHN rather than TET at the short reaction time (5 min.). TET converted very little and only formed small amounts of NAP.

Argonne Coals. Cyclic olefins have been shown to be effective hydrogen donors for bituminous coals, Western Kentucky (Bedell and Curtis, 1991) and for Pittsburgh No. 8 coal. To establish the universality of these donors, a series of reactions was performed in which cyclic olefins were reacted with eight coals from the Argonne Premium Coal Sample Bank. The efficacy of the hydrogen donation from the cyclic olefins to coals of different rank was compared to the efficacy of hydrogen donation from hydroaromatic donors. These reactions were performed using an equivalent amount of donable hydrogen for each hydrogen donor species and a reaction time of 30 minutes. The efficacy of hydrogen donation for each hydrogen donor for each coal was evaluated in terms of coal conversion to THF solubles.

The coals, themselves, had considerably different reactivities. Reactions in hydrogen and hexadecane without an added hydrogen donor ranked the reactivity of the coals for conversion as Illinois No. 6 > Western Kentucky No. 9 > Pittsburgh No. 8 > Blind Canyon > Wyodak-Anderson and Upper Freeport > Beulah-Zap and Lewiston-Stockton >> Pocahontas No. 3. The reactivity ranking of the coals became less distinct when the different donors were added to the reaction system. The addition of hydrogen donors to the system increased the amount of coal conversion obtained for most of the coals. The most active donors were the cyclic olefins, HHA and ISO, and the hydroaromatic donor, DHA. The hydroaromatic donors, OHA and TET, contributed less hydrogen to the system and resulted in less coal conversion.

The coals of high inherent reactivity, Kentucky No. 9, Illinois No. 6, and Pittsburgh No. 8 showed similar coal conversions with DHA and HHA. These coals were evidently sufficiently

reactive to be able to utilize the hydrogen that was quickly released from the cyclic olefin, HHA. The coals of lower reactivity, Upper Freeport, Lewiston-Stockton, Blind Canyon, Wyodak, and Beulah Zap, showed a much wider disparity between the coal conversion obtained with DHA and that from HHA. For these coals, the quick release of hydrogen from HHA was not effective in promoting coal conversion, most probably because these coals were slow to react and could not utilize the hydrogen released from the cyclic olefin quickly enough to promote coal conversion.

SUMMARY

The combination of the cyclic olefin, HHA, with the hydroaromatic donor, DHA, was the most effective hydrogen donor system, producing the most coal conversion in the least amount of time. HHA released its hydrogen rapidly to produce high initial levels of coal conversion to THF solubles. Although coal conversion increased with increasing reaction time, the combined HHA/DHA yielded a high level of coal conversion at very short time with only small increases being observed with increased time. The high level of reactivity of the cyclic olefins resulted in quick release of hydrogen that could then be incorporated into the dissolving coal matrix of the reactive coals. However, the coals of lesser reactivity did not benefit to nearly the same degree to the quick release of the hydrogen by the cyclic olefin. The slower release of DHA was more effective in promoting the desired reactions between donated hydrogen and the less reactive coals.

REFERENCES

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Table 1. Effect of Hydrogen Donor Content on Coal Conversion

Percentage of Hydrogen Donor		Coal Conversion
Dihydroanthracene	Hexahydroanthracene	
%	%	%
100	0	56.4 ± 0.1
75	25	60.8 ± 1.6
50	50	63.7 ± 0.1
25	75	55.5 ± 0.3
0	100	51.8 ± 0.6
0	0	20.1 ± 3.3

Reaction Conditions: Pittsburgh No. 8 coal, hexadecane as solvent, 1250 psig H₂ at ambient temperature, 380°C, 30 minute reaction time.

Table 2. Effect of Time and Hydrogen Donor Content on Coal Conversion

Hydrogen Donor	Coal Conversion (%) at Specific Reaction Times (min)			
	5	15	30	60
HHA + DHA ^a	30.9±0.3	58.0±0.5	63.1±1.0	63.7±0.1
DHA	27.5±1.1	55.2±0.3	56.4±0.1	67.7±1.6
HHA	32.3±1.4	44.6±4.0	51.8±0.6	65.0±0.7
OHA	15.5±1.2	25.9±0.9	38.8±1.0	58.5±0.9
ISO	19.1±0.6	37.1±1.6	42.3±5.2	58.8±0.2
TET	6.0±0.4	17.4±1.0	30.5±3.8	56.9±2.6
No Donor	7.9±0.2	20.9±0.1	20.1±3.3	44.2±3.1

Reaction Conditions: Pittsburgh No. 8 coal, hexadecane as solvent, 1250 psig H₂ at ambient temperature, 380°C.

^aHHA and DHA present in a 1 to 1 weight ratio.

Table 3. Proximate Analysis of the Argonne Premium Sample Coals

Coal	Moisture %	Ash %	Volatile Matter %	Sulfur %	BTU	Rank
Kentucky No. 9	7.12	10.97	35.77	4.50	11936	HVB
Illinois No. 6	7.97	14.25	36.86	4.45	10999	HVB
Upper Freeport	1.13	13.03	27.14	2.29	13315	MVB
Pocahontas No. 3	0.65	4.74	18.48	0.66	14926	LVB
Pittsburgh No. 8	1.65	9.10	37.20	2.15	13404	HVB
Lewiston Stockton	2.42	19.36	29.44	0.69	11524	HVB
Blind Canyon	4.63	4.49	43.72	0.59	13280	HVB
Wyodak	28.09	6.31	32.17	0.45	8426	Sub B
Beulah Zap	32.24	6.59	30.45	0.54	7454	LIG

All values are weight percents for the as-received coals.

HVB = high volatile bituminous
MVB = medium volatile bituminous
LVB = low volatile bituminous
Sub B = subbituminous
LIG = lignite

Table 4. Coal Conversion for Reactions of Argonne Coals with Hydrogen Donors in Hexadecane

Coal Reacted	Coal Conversion: (%) with					
	DHA	HHa	OHA	ISO	TET	No Donor Added
Kentucky No. 9	68.3(1.0)	65.0(3.3)	49.7(1.0)	37.2(0.4)	29.8(0.2)	25.6(1.8)
Illinois No. 6	69.6(2.0)	67.7(0.2)	66.1(2.8)	65.5(1.6)	62.1(2.0)	55.7(0.1)
Upper Freeport	47.1(2.0)	15.8(1.2)	13.0(1.7)	20.9(2.5)	8.3(0.7)	11.4(0.5)
Pocahontas No. 3	4.5(0.1)	-4.4(0.1)	-6.1(2.0)	-6.7(1.5)	-3.1(1.0)	-5.7(1.7)
Pittsburgh No. 8	56.4(0.1)	51.8(0.6)	38.8(1.0)	42.3(5.3)	30.5(3.8)	20.1(3.3)
Lewiston Stockton	41.7(1.9)	25.2(2.1)	19.6(1.2)	20.9(1.1)	9.1(2.6)	6.0(3.1)
Blind Canyon	64.8(3.9)	41.6(1.6)	27.9(0.7)	25.3(0.2)	15.2(2.0)	17.4(0.4)
Wyodak (dried)*	50.6(0.6)	40.5(1.3)	21.4(1.2)	21.1(2.9)	14.9(1.5)	11.7(1.5)
Beulah Zap (dried)*	35.6(3.0)	20.8(3.0)	13.3(1.0)	13.8(0.1)	5.0(2.5)	8.1(2.1)

Reaction Conditions: hexadecane as solvent, 1250 psi, hydrogen at ambient temperature, 30 minute reaction time, 380°C
 * dried to approximately 4% moisture content